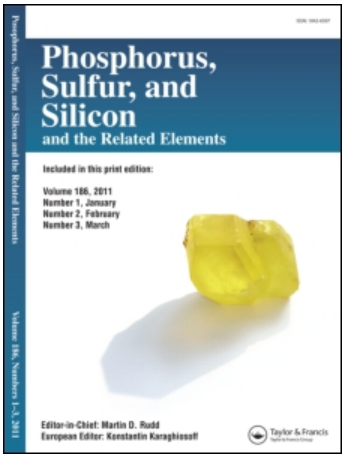

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Phosha-Meerwein Reaction of Diazo Esters

Konstantin A. Popov[a]; Alexander M. Polozov[a]
[a] A.M. Butlerov Research Chemical Institute, Kazan State University, Kazan, Russian Federation

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PHOSHA-MEERWEIN REACTION OF DIAZO ESTERS

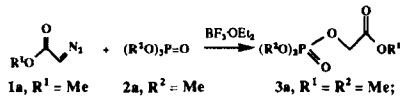
KONSTANTIN A. POPOV and ALEXANDER M. POLOZOV*
A.M. Butlerov Research Chemical Institute, Kazan State University, Lenin Str., 18,
Kazan 420008, Russian Federation

Abstract.

Diazo esters (**1a,b**) react with trialkyl phosphates (**2a-c**) in the presence of $BF_3{\cdot}OEt_2$ to give the corresponding phosphates (**3a-c**) in 42-58 % yields. The competed intra/intermolecular protonation in the reaction of **1a** with dimethyl hydrogen phosphite leads to phosphonate **4** and phosphite **5**.

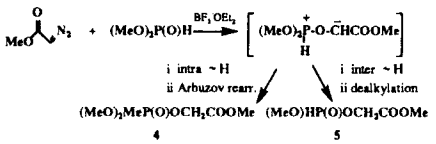
Key Words: Diazo ester; dimethyl hydrogen phosphite; Lewis acid catalysis; phoshate; zwitterionic phosphonium intermediate.

We have found that diazo esters (**1a,b**) react with trialkyl phosphates (**2a-c**)) in the presence of $BF_3{\cdot}OEt_2$ (10 Mol %) to give the corresponding phosphates (**3a-c**) in 42-58 % yields.



1a, R^1 = Me **2a**, R^2 = Me **3a**, $R^1 = R^2$ = Me;
1b, R^1 = Et **2b**, R^2 = Et **3b**, $R^1 = R^2$ = Et;
2c, R^2 = i-Pr **3c**, R^1 = Et, R^2 = i-Pr

The catalytic capability of a set of catalysts indicates a Lewis acid promoted process: $BF_3{\cdot}OEt_2$ (52 %) > $(p\text{-}Br\text{-}C_6H_4)_3N^+{\cdot}SbCl_6^-$ (35 %) > $SnCl_2$ (17 %) > $Rh_2(OAc)_4$ (14 %) > $Cu(OTf)_2$ (5 %) (**3a**). Using CD_2Cl_2, D_2O, $(CD_3O)_3PO$ and $N_2CDCOOCH_3$, the reaction is explained by a step mechanism *via* zwitterionic phosphonium intermediate, followed by protonation at C atom by H_2O impurities and dealkylation at P atoms.



The competed intra/intermolecular protonation in the reaction of **1a** with dimethyl hydrogen phosphite leads to mixtute of phosphonate **4** and phosphite **5**, whereas in the presence of large excess of **1a** a product of complete replacement, $(MeOOCH_2O)_2P(O)Me$ has been isolated, arose from both **4** and **5**.